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(56) Documents cited
GB 1437993 A GB 1365744 A EP 0219163 A

(58) Field of search
UK CL (Edition L) C5E EAS EAT
INT CL[5] C01B

(54) **Process for producing hydrogen and/or carbon monoxide**

(57) In a non-catalytic process for production of gases essentially comprising hydrogen and/or carbon monoxide from hydrocarbon-containing gases by contacting the latter gases with a heated bed of solids, with endothermic hydrocarbon cracking and/or water gas reaction steps by alternating combinations of exothermic and endothermic reactions via said solids, the hydrocarbon-containing gases are flash-heated to the desired reaction temperature of 950–1200°C, by contact with a recycled stream 5 of hot product gases.

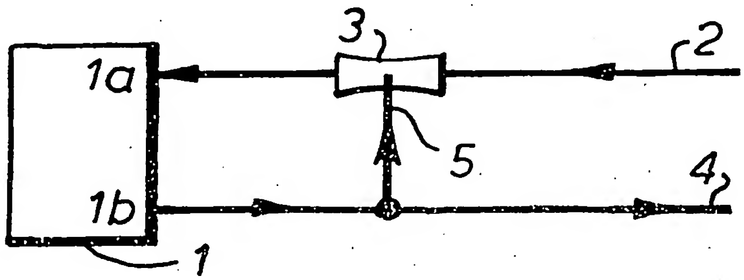

FIG.1

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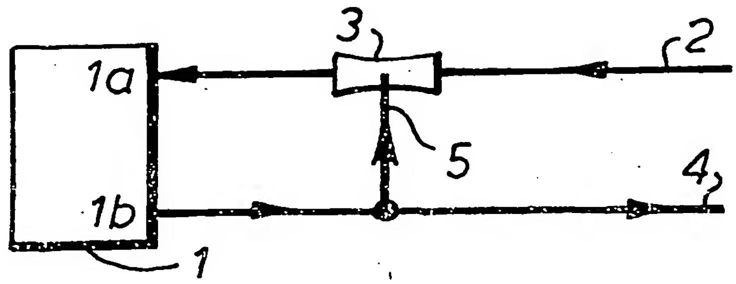

FIG.1

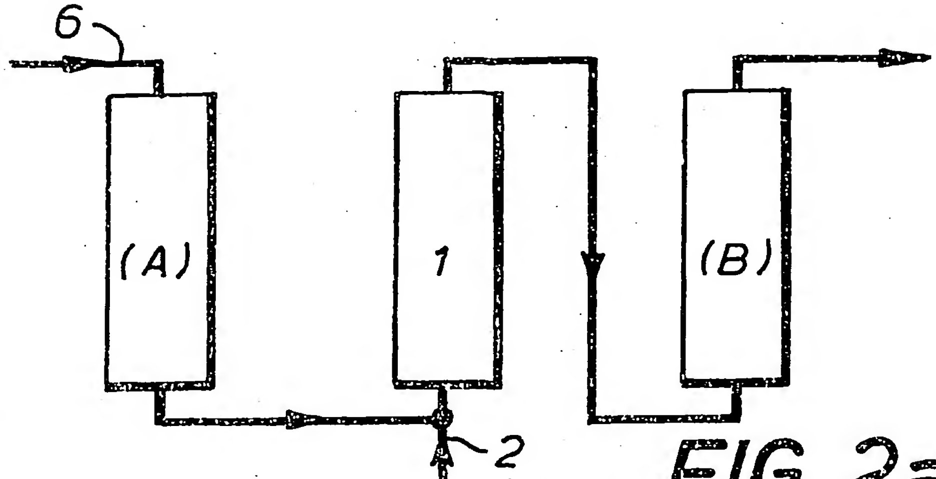

FIG. 2a

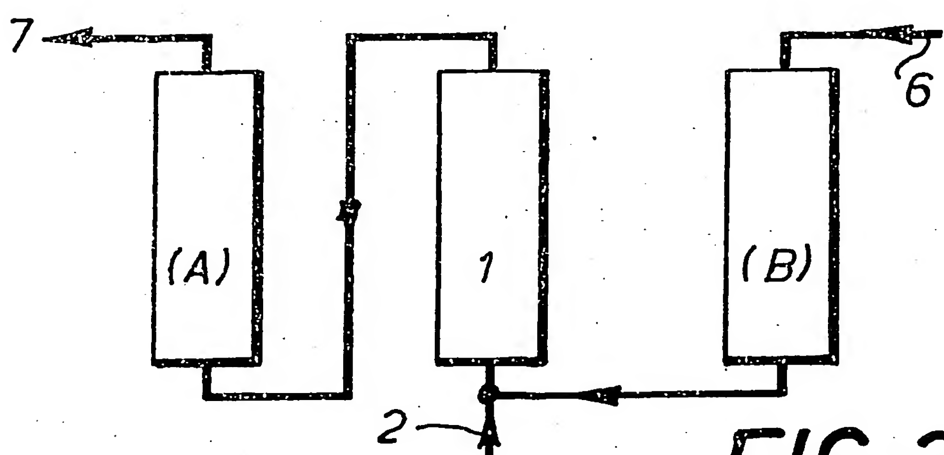

FIG. 2b

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PROCESS FOR PRODUCING A HYDROGEN-CONTAINING GAS

The present invention relates to a non-catalytic process for producing a hydrogen-containing gas, wherein use is made of direct heat exchange via high temperature heat storage in refractories.

In particular, the invention relates to a non-catalytic process for producing a hydrogen-containing gas and/or synthesis gas from gaseous hydrocarbons such as e.g. methane, natural gas, associated gas, (i.e. gas produced together with oil in production fields), naphtha etc. in regenerator-type reactors. In such reactors which comprise heated solids, alternating combinations of exothermic and endothermic reactions are carried out in such a manner that the desired reactions:

$CH_4 \longrightarrow C + 2H_2$ and/or

$C + H_2O \longrightarrow CO + H_2$ and/or

$CH_4 + H_2O \longrightarrow CO + 3H_2$

will occur.

However, when using regenerator-type reactors for the production of hydrogen-containing gases, one is faced with the problem that the hydrocarbon-containing feed gases have to be heated to the desired reaction temperature of 1000-1200 °C.

However, above a temperature of 400-600 °C cracking of the hydrocarbon-containing feed gases will start leading to the formation of tarry and sooty material which is interfering with the desired process conditions through plugging of the equipment applied.

Thus, it is an object of the invention to provide a process for production of a hydrogen-containing gas from hydrocarbon-containing gases using a regenerator-type reactor, wherein the above problems are avoided.

The invention therefore provides a non-catalytic process for production of gas essentially comprising hydrogen and/or carbon monoxide from hydrocarbon-containing gas by contacting the latter

gas in a regenerator-type reactor with a bed of solids with endothermic hydrocarbon cracking and/or water gas reaction steps, by alternating combinations of exothermic and endothermic reactions via said solids in regenerator-type reactors, characterized in that the hydrocarbon-containing gas is flash-heated to the desired reaction temperature of 950-1200 °C.

Flash heating is herein defined as a process in which relative cold gases are heated in a very short time by mixing with very hot gases.

The invention will now be described by way of example in more detail by reference to the accompanying drawings, in which: Fig. 1 represents schematically the principle of the invention; and Figs. 2a, b represent schematically an advantageous application of the process of the present invention.

Referring now to Fig. 1, a regenerator-type reaction stove 1 is shown, in which stove the endothermic and exothermic reactions described in the foregoing are carried out.

Regenerator-type stoves as such are known to those skilled in the art from e.g. blast furnaces and will therefore not be described in detail.

Generally, it can be said that such a stove is a vessel comprising a bed of solids which are alternately heated up and cooled down, dependent on whether exothermic or endothermic reactions are carried out.

Advantageously the stove is largely filled with a "checker" work consisting of stacked high temperature resistant refractory bricks with holes in them through which the gases flow. The stoves are operated in two cycles. For blast furnaces hot flue gases heat the checker in downflow. During the heating cycle and during the cooling cycle the checker in turn heats the upward flow of air for the blast furnace. During this cycle the stove is operated at the pressure of 3-5 bar. By a proper sequence control the temperature of the air is held constant at 1290-1320 °C.

The process according to the invention is suitably carried out in one or more fixed beds comprising a heated mass of solids. Fixed

beds could be applied which may contain heat-resistant solid material in any desired shape and size, such as a fixed brick matrix or a packed bed of particulate solids. Particulate solids such as packed spheres or cylinders with main dimensions (e.g. diameter, height of the cylinder) of 1-50 mm, and in particular 2-50 mm, are suitably used in the present process.

Various solid materials may be used in the process according to the present invention provided that the material is sufficiently heat-resistant and can withstand large temperature variations which occur during start-up and shut-down of the process. Suitable solids comprise refractory oxides, silicium carbide, carbonaceous materials (e.g. petrol cokes) and mixtures thereof. Metal alloys or metal compounds may also be suitably used; these materials have the advantage of possessing a relatively high thermal conductivity and volumetric heat capacity compared with the previously mentioned materials. In some cases it may be advantageous to use solids which, as such or in the form of additional compounds, possess catalytic activity for at least one of the process steps. However, in most cases substantially non-catalytic solids will be most suited for use in the process according to the invention because the deposition of carbon on the surface of the solids will usually lead to a substantial decrease in catalytic activity, if present in fresh solids. Advantageously, the bed of solids comprises alumina beads.

Preheating of the solids applied in the process according to the invention to any temperature suitable for the purpose may be carried out in various ways. Advantageously, the solids are preheated to a temperature of 1400-1650 °C before being contacted with the hydrocarbon-containing gas. Suitably the solids are heated by combustion under pressure of a fuel gas with an oxygen-containing gas and contacting the combustion gas with the solids, whereafter the combustion gas is cooled e.g. by preheating the hydrocarbon-containing gas and/or air.

Various gaseous hydrocarbonaceous materials can be used as feed for the process according to the invention. In particular

natural gas. methane, associated gas, LPG and evaporated naphtha are used. In some cases natural gas is preferably subjected to a treatment to remove sulphur and/or inorganic substances before using it as feed for the present process.

Via an inlet 1a at the top of the stove 1 hydrocarbon-containing feed gases which usually are preheated from ambient temperature to 500 °C in an indirect heat exchanger (not shown for reasons of clarity), are introduced into the stove 1 through any line 2 suitable for the purpose and an ejector-type compressor 3, which ensures rapid mixing and is suitable to be applied in a hot environment. Such compressors are known to those skilled in the art and will not be described in detail.

The product gas is discharged from the stove 2 via any suitable outlet 1b at the bottom and any line 4 suitable for the purpose for further suitable processing.

After starting the process by heating the stove in any suitable manner, the gaseous hydrocarbons are flash-heated through the disadvantageous temperature zone to a temperature range where the above desired endothermic reactions occur, by recycling at least part of the hot product gases through any suitable recycle line 5 to the feed line 2 and the compressor 3, so that a reaction mixture comprising feed gases and hot recycled product gas is supplied to the inlet 1a.

The following non-limiting Example can be referred to: a quantity of 214.2 Ton/hr of hydrocarbon-containing feed gas is supplied to the compressor 3 via the feed line 2 at a temperature of 500 °C and at a pressure of 11 bar.

When recycling, 547.0 Ton/hr of gaseous hydrocarbons are supplied from the compressor 3 to the inlet 1a at 1000 °C and a pressure of 7.50 bar, whereas 547.0 Ton/hr of hot product gas at 1281 °C and 7.47 bar is discharged from the outlet 1b and subsequently is splitted into 332.8 Ton/hr of recycled gas at 1281 °C in line 5 and 214.2 Ton/hr of product gas at 1281 °C and 7.47 bar in line 4.

An additional advantage of the above line up is that the temperature profile in the stove can be controlled within narrow ranges. In this way problems as too low cut off temperatures during the heating of the stove can be avoided.

Figs. 2a and b represent block schemes of an advantageous embodiment of the invention wherein for heating of the reaction stove(s) use is made of a flue gas heat recovery stove as used in e.g. glass ovens. Such heat recovery stove are operating in a cyclic manner similar to that described earlier with respect to the blast furnace-type reactor. The process sequence is then as follows. In Fig. 2a (representing the heating cycle) combustion air supplied via any suitable line 6 to a heat recovery stove (A) is preheated in the heat recovery stove (A) to about 1000 °C. By burning some fuel gas such as hydrogen supplied via any suitable line 2 to the reaction stove 1 with this air a flue gas is formed with a temperature of 1300 °C which is used for heating the reaction stove 1. After the top heat between e.g. 1000 °C and 1300 °C has been used for heating the reaction stove 1 the remaining heat in the flue gas is used to preheat a second heat recovery stove (B). In the cooling cycle the said heat between 1000 °C and 1300 °C is then used to accomplish the endothermic reforming reactions leading to cooling down the stove, after which the reaction stove 1 is heated again in a heating cycle during which procedure the combustion air is heated in stove (B) and stove (A) is heated with the flue gas leaving the reaction stove 1 etc. (see Fig. 2b).

Reference number 7 represents the flue gas to the stack from the second preheated heat recovery stove. In Figs. 2a and b the same reference numerals have been used.

To those skilled in the art it will be clear that in order to obtain a continuous flow of product gas at least two reaction stoves are required and at least 2 heat recovery stoves. Proper sequencing will then result in a more or less continuous flow of product gas, flue gas and preheated combustion air.

Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description. Such modifications are intended to fall within the scope of the appended claims.

CLAIMS

1. A non-catalytic process for production of gas essentially comprising hydrogen and/or carbon monoxide from hydrocarbon-containing gas by contacting the latter gas in a regenerator-type reactor with a bed of solids, with endothermic hydrocarbon cracking and/or water gas reaction steps, by alternating combinations of exothermic and endothermic reactions via said solids in regenerator-type reactors characterized in that the hydrocarbon-containing gas is flash-heated to the desired reaction temperature of 950-1200 °C.

2. The process as claimed in claim 1, characterized in that the flash-heating is accomplished by contacting the hydrocarbon-containing gas at a temperature between 400 and 600 °C with at least part of the hot product gas having a temperature above 1200 °C.

3. The process as claimed in claim 2, characterized in that at least part of the hot product gas is recycled to the regenerator-type reactor.

4. The process as claimed in claim 3, characterized in that the hot product gas recycling takes place via an ejector-type compressor.

5. The process as claimed in any one of claims 1-4, characterized in that the hydrocarbon-containing gas is chosen from methane, natural gas, associated gas, or naphtha.

6. The process as claimed in any one of claims 1-5, characterized in that the bed of solids is heated by means of one or more flue gas heat recovery stoves.

7. Hydrogen-containing gas whenever obtained by the process as claimed in any one of claims 1-6.

8. Carbon monoxide-containing gas whenever obtained by the process as claimed in any one of claims 1-6.

VM7/T6153FF

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number: GB 9305909.5

Relevant Technical fields

(i) UK Cl (Edition L) C5E (EAS EAT)

(ii) Int Cl (Edition 5) C01B

Databases (see over)

(i) UK Patent Office

(ii)

Search Examiner: R J WALKER

Date of Search: 12 MAY 1993

Documents considered relevant following a search in respect of claims 1-8

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1437993 A (NIPPON KOKAN KK) See eg Page 3 Line 109 Page 4 Line 20	At least 1,5,6,7,8
X	GB 1365744 A (NIPPON KOKAN KK) See Page 1 Line 78 Page 2 Line 5 Page 2 Lines 60-66	At least 1,5,6,7,8
A	EP 0219163 A (SHELL INTERNATIONALE RESEARCH) See whole document	At least 1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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